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AIR POLLUTANTS FROM SURFACE MATERIALS: FACTORS INFLUENCING EMISSIONS, AND PREDICTIVE MODELS

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Abstract

The purpose of this paper is to present an overview of the present state of knowledge of emissions from surface materials, the factors that influence those emissions, and models that can be used in evaluating emissions data. It concludes by focusing on indoor air quality control by controlling emissions, especially by producing and using low-emitting materials.

Introduction

Many indoor air pollutants come from evaporation or sublimation from surfaces of indoor materials. These "material" sources of indoor air pollutants include any substances that form the building itself or its contents. Other types are "combustion" sources, such as vented or unvented space heating devices; "activity" sources that involve human activities, such as maintaining, cooking, using aerosol spray products, and using machines; and "outside" sources, such as infiltrated air and contaminated soil gas.

Whereas indoor pollutants from surface materials can be inorganic and particulate in nature, vapor-phase organic chemicals generally predominate in terms of mass concentration and chemical variety. Typical indoor concentrations of organic vapors range from tens to thousands of micrograms per cubic meter; tens to hundreds of different compounds are typically measureable. While surface materials are not the only sources of these compounds, they are usually significant contributors.

Emissions from Surface Materials

The types of materials in typical residential and office buildings cover a wide variety of building materials and contents. They range from materials with virtually no emissions (which may in fact act as adsorbers, or "sinks" for pollutants) to large surface area, high emission

rate materials with sufficient content of volatilizable compounds to contaminate indoor air and irritate occupants for long periods.

In addition to emission rate, a measure often referred to as "source strength," materials can also be characterized by the duration of their emissions. Some materials have an essentially constant emission rate. Examples include moth crystals that at room temperature emit paradichlorobenzene at a nearly constant rate until the crystals are gone, and certain types of aged particleboard that have emission rate half-times of a year or more. Other materials have a slow-decay emission rate. These materials have emission rate half-times of weeks or months. Examples include certain types of floor and wall coverings and furniture. A third category is rapid-decay emission rate materials. These have emission rate half-times of minutes, hours, or days. Many "wet" materials such as paints, polishes, and adhesives have such characteristics for a period after they have been applied.

Controlled studies of the rates and compositions of emissions from representative materials help to understand the potential impact of these sources on indoor air quality, and the options for controlling their impacts. Such research studies were begun in Europe about 10 years ago, and more recently in North American laboratories.

The most common approach for such studies has been to put samples of materials in chambers through which controlled amounts of clean air are passed. Concentrations of emitted pollutants in the air exiting from the chambers are measured. In the most detailed studies, emissions are measured as a function of time (age of material), temperature, air flow rate, area of sample per unit volume of chamber, and relative humidity.

In North America, guidelines on procedures for testing organic compound emissions from indoor sources are under development by the American Society for Testing and Materials (ASTM). These guidelines will recommend procedures to use in research studies conducted in small laboratory apparatus, small chambers, large chambers, and actual buildings. Procedural guidance will cover equipment specifications, experimental design, sampling and analysis, data analysis, and quality assurance (1).

More routine testing procedures, for either product certification by manufacturers or product screening by purchasers, are less developed. The current intention within the indoor air research community is to first get consensus on research procedures, and then develop simplified versions for routine product testing.

Although difficult to conduct and moderately expensive, such chamber studies are less expensive and more controllable than studies in actual buildings. If chamber data can be modeled to simulate emissions from materials under a wide range of environmental conditions, and further modeled to predict indoor concentrations and exposures, chamber studies and modeling will become valuable tools for design and selection of indoor materials.

Factors Influencing Emissions

The major factors that are now thought to influence emission of vapor-phase organic compounds from surface materials are: (a) total content of vaporizable constituents in the material; (b) distribution of these constituents between the surface and the interior of the material; (c) age of the material; (d) surface area of the material per volume of the space it is in ("loading"); and (e) environmental factors such as temperature, air exchange rate, and relative humidity. (Local air velocity near the surface of the material, and material surface details, undoubtedly have an effect for some materials, but controlled studies of this effect have not been reported in the indoor air quality literature.)

For a given material, research studies of emission rates should account for time (age), temperature, and air exchange rate. Early research studies of formaldehyde emissions from pressed-wood products showed that relative humidity was also an important factor. However, research studies of other pollutants have shown that their emission rates from various materials are not particularly sensitive to relative humidity, at least for the normal range found indoors. Therefore, only materials that are known to emit highly polar compounds need to be tested at different relative humidities.

Source (Emission) Models

Mathematical models are under development that relate emission rates for various types of materials to the major factors influencing emissions. The earliest efforts to do this were for formaldehyde emissions from pressed-wood products. One model (5) shows that the emission rate of formaldehyde from these products is primarily a function of temperature, relative humidity, and concentration of formaldehyde in the air (which is, in turn, a function of loading).

Source modeling has been extended by others who are concerned about a greater variety of pollutants and materials. One type of model based on small-chamber testing of materials accounts for the effects of air exchange, loading, and time, but does not account for temperature or humidity effects. For constant emission rate materials, this type of model is simply:

$$EF = C(Q/A) \text{ or } EF = C(N/L) \qquad (1)$$

where EF = emission factor for any compound or a group of compounds, mg/h per m^2 of surface material

C = concentration in outlet air from chamber, mg/m^3

Q = air flow through chamber, m^3/h

A = area of material in chamber, m^2

N = air exchange rate through chamber, h^{-1}

L = loading of surface material in chamber, m^2/m^3

For most purposes, slow-decay emission rate materials are modeled in the same way, except through a series of constant emission factors stepped down at appropriate points in time.

Rapid-decay emission rate materials require models that consider time. One current model (9) assumes that the test chamber is an ideal continuous stirred tank reactor, and that the emission rate decay is first-order. Its basic form is:

$$EF = EF_o e^{-kt} \qquad (2)$$

where EF = emission factor, mg/m^2-h

EF_o = initial emission factor, mg/m^2-h

e = base of natural logarithms

k = first-order rate constant, h^{-1}

t = time, h

Both the initial emission factor and the rate constant are influenced by air exchange rate and material loading in the chamber. Values for EF_o and k are obtained by non-linear regression curve-fitting of the concentration versus time data from chamber experiments.

More comprehensive models that account for all additional significant factors influencing emissions -- which can include temperature, the "sink" effects of absorbing indoor materials, and in certain cases relative humidity -- have been developed for research purposes (3), but are not likely to be applied to practical situations in the near future. The experimental work required to support their development and subsequent use is too expensive. A more practical approach will be to determine the two (at most, three) factors that have the greatest influence on emissions for a particular type of material, and develop a specific model that accounts for those two or three factors. Such source models will be quite sufficient for their two main uses: as inputs to indoor air quality predictive modeling, and as guidance on the most effective way to "condition" (i.e., accelerate the emissions from, and decrease the residual volatiles in) materials at the point of manufacture or use.

Using Emissions Data

There are two general uses of emissions data: evaluating risks for research or regulatory policy decisions, and designing or selecting materials to ensure good indoor air quality. Public health officials can use emissions data to evaluate the exposure or health risks of sources. These risk evaluations lead to research priorities, or decisions on whether public guidance on source use or regulation of a material is needed.

Building designers, builders, and managers can make similar use of emissions data, although their decisions are of different types. They can use such data in the selection of materials to use, and in the operation of building ventilation systems (especially when buildings are new or newly renovated, and apt to have large amounts of new surface materials with volatile organic residuals).

Manufacturers of materials can use emissions data to design inherently low-emitting materials, ensure quality control during production, and develop guidelines for end users on conditioning their materials (to remove residual volatiles).

The traditional use of emissions data is in indoor air quality (IAQ) models that predict indoor concentrations of the emitted pollutants. IAQ predictive models can be as simple as well-mixed equilibrium box models that equate indoor concentrations directly to source emission rate, building volume affected by the emissions, and air exchange between the affected volume and other spaces, including outdoors. Personal computer-based models are now becoming available (2, 7) that can handle time varying sources and ventilation conditions. These are especially useful for evaluating IAQ control options.

Such calculations can be especially useful if there is an indoor concentration, or concentration range, that is accepted as undesirable to exceed. Public health officials and researchers can use such calculations for source comparisons, and manufacturers can use them to judge whether their products are likely to be acceptable from an IAQ standpoint.

A simplified example of emissions data use is illustrated in Table 1 and Figure 1. Typical emission factors for vapor-phase organic compounds from a variety of surface materials — and, for general comparison, some combustion sources and aerosol spray products -- are listed in Table 1. They were selected as illustrative, rather typical values from IAQ research studies. A typical application factor for residential use was then applied to obtain emission rates in milligrams per hour.

Figure 1 shows these emission rates, on a logarithmic scale, in a simple bar chart. The chart also has two horizontal lines, at emission rates of 1000 mg/h (log 3) and 100 mg/h (log 2). These lines correspond roughly to emission rates that in a typical house of 300 m^3 and 0.5 air

Table 1. Typical emission rates for sources of vapor-phase organics in residences (total vapor-phase organic compounds, except as noted).

Label	Source*	Condition	Emission factor**	Assumed amount	Emission rate (mg/h)
	Material Sources				
A	Silicone caulk	<10 hours	13 mg/m^2-h	0.2 m^2	3
A'	Silicone caulk	10-100 hours	<2 mg/m^2-h	0.2 m^2	<0.4
B	Floor adhesive	<10 hours	220 mg/m^2-h	10 m^2	2200
B'	Floor adhesive	10-100 hours	<5 mg/m^2-h	10 m^2	<50
C	Floor wax	<10 hours	80 mg/m^2-h	50 m^2	4000
C'	Floor wax	10-100 hours	<5 mg/m^2-h	50 m^2	<250
D	Wood stain	<10 hours	10 mg/m^2-h	10 m^2	100
D'	Wood stain	10-100 hours	<0.1 mg/m^2-h	10 m^2	<1
E	Polyurethane wood finish	<10 hours	9 mg/m^2-h	10 m^2	90
E'	Polyurethane wood finish	10-100 hours	<0.1 mg/m^2-h	10 m^2	<1
F	Floor varnish or lacquer		1 mg/m^2-h	50 m^2	50
G	Particleboard	2 years old	0.2 mg/m^2-h	100 m^2	20
G'	Particleboard (HCHO)	new	2 mg/m^2-h	100 m^2	200
H	Plywood paneling (HCHO)	new	1 mg/m^2-h	100 m^2	100
I	Chipboard		0.13 mg/m^2-h	100 m^2	10
J	Gypsum board		0.026 mg/m^2-h	100 m^2	3
K	Wallpaper		0.1 mg/m^2-h	100 m^2	10
L	Moth cake (para)	23 °C	14,000 mg/m^2-h	0.02 m^2	280
	Combustion Sources				
M	Unvented gas burner		85-144 mg/h	1 burner	100
N	Unv. gas space heater (HCHO)	radiant	0.001 mg/kJ	20,000 kJ/h	20
O	Unv. kerosene space heater	convective/ radiant	0.007 mg/kJ	6100 kJ/h	45
P	Unv. kerosene heater	radiant/ radiant	0.064 mg/kJ	9400 kJ/h	600
Q	Cigarette smoking	one smoker	10 mg/cig.	2 cig./h	20
	Activity Sources				
R	Hair spray	6-sec. use	3 mg/use	1 use/h	3000
R'	Hair spray	6-sec. use	3 mg/use	1 use/day	120
S	Disinfectant spray	6-sec. use	5 mg/use	1 use/h	5000
S'	Disinfectant spray	6-sec. use	5 mg/use	1 use/day	210

Notes

* Emissions data shown are typical only for the specific brands, models, or units that have been tested; the data do not represent all products of the source type listed. Product-to-product variability can be very high.

** Typical values selected by author based on data in a database on the sources of indoor air pollution emissions (reference 11).

Label = source type label on Figure 1
Para = paradichlorobenzene
HCHO = formaldehyde

changes per hour would respectively lead to house-wide concentrations well above and well below 1000 ug/m^3. The 1000 ug/m^3 concentration is simply a single-source maximum contribution that might be advisable, based on the work of Mølhave (6), which suggests that concentrations of less than 5,000 ug/m^3 of total vapor-phase organics can be irritating to some people. This is a concept proposed earlier (10) as interim guidance to building designers, owners, and product manufacturers until more definitive health response data from exposure to low-level organics become available.

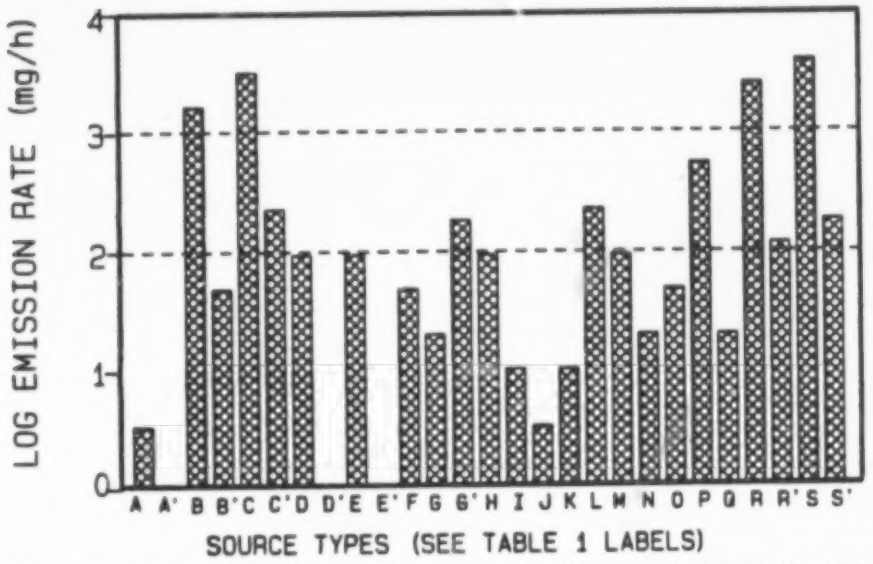

FIGURE 1. TYPICAL EMISSION RATES IN RESIDENCES (TOTAL VAPOR-PHASE ORGANIC COMPOUNDS)

As an example, the particular floor adhesive and floor wax in Figure 1 have average emission rates well above the upper bound of apparent concern during the first 10 hours after they are applied. The aerosol disinfectant and hair sprays, for the use conditions assumed, are also above the upper line. Some products fall in the "grey zone" between 100 and 1000 mg/h, and most of the products shown fall below the lower level of apparent concern. In principle, plots such as Figure 1, constructed around various health endpoints, can identify major sources of any pollutants of concern and can guide manufacturers on the indoor air suitability of their products.

An extension of such plots, taking into consideration the duration of emissions (when experimental data are available on emission rates over time), can be used to evaluate the possible benefits of conditioning materials. Such conditioning, also referred to as "airing out" and "baking out," can be done at the point of manufacture; after purchase but

before installation in a building; after installation but before occupancy; or (least desirably) after a new or renovated building has been occupied and found to have unacceptable indoor air quality. Again in principle, because these concepts have not been tested extensively in practice, emissions data can be used to make decisions on when and where to condition surface materials with high emission rates.

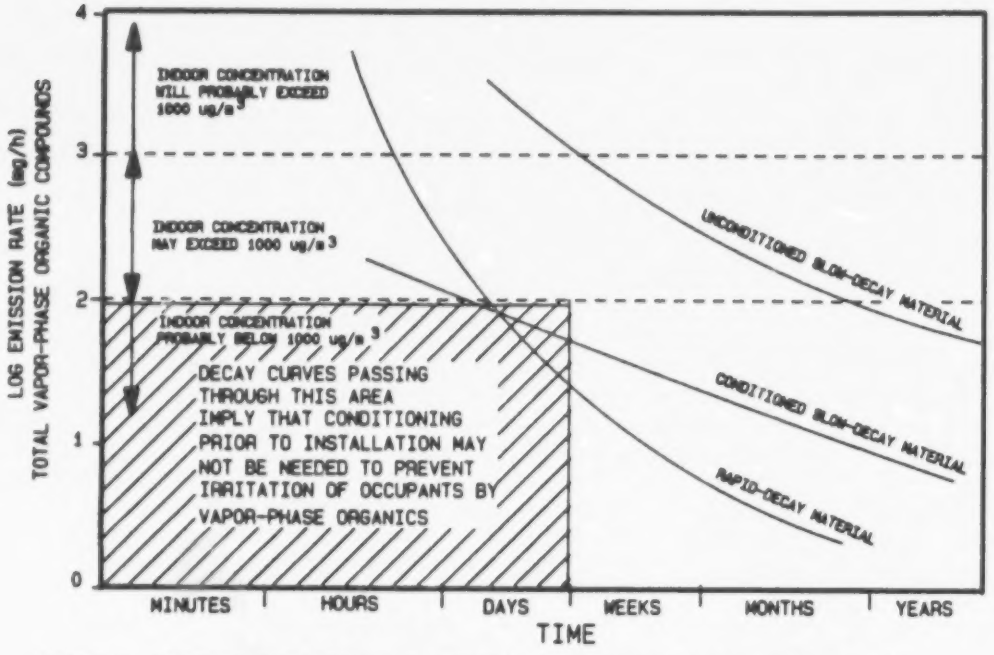

FIGURE 2. EMISSION RATE DECAY AND MATERIAL CONDITIONING (ILLUSTRATION OF A CONCEPT; EXAMPLE BASED ON RESIDENTIAL SITUATIONS, AND OCCUPANT IRRITATION BY VAPOR-PHASE ORGANIC COMPOUNDS)

Figure 2 illustrates an approach to making decisions on conditioning. It has the same scale and acceptability levels of emission rates as Figure 1. Again, the values are based on typical residential space and ventilation conditions. This figure, however, has a general time scale that allows presentation of emission decay rates in terms that are meaningful to decisions on conditioning. The "rapid-decay material" curve is typical of substances like the floor adhesive and floor wax in Table 1 and Figure 1. The decay is sufficiently rapid that conditioning of the material (or reformulating a coating material like an adhesive or wax) prior to installation or use may not be necessary. Although the emissions are initially very high, it is only a matter of hours or days before indoor concentrations are likely to be in an acceptable range. Some type of conditioning of the building after application but before occupancy might be prudent, however.

The "unconditioned slow-decay material" also has a high initial emission rate. If the acceptability limits on emission rates are applicable, this material is likely to lead to complaints, perhaps for months or longer. It is therefore a candidate for conditioning prior to installation. Chamber tests can show which factors (e.g., temperature, air exchange, and time for airing out; or some treatment of the material such as cleaning) will accelerate emissions and deplete the residual volatile compounds most effectively. The goal would be to lower the emission characteristics to something like the "conditioned slow-decay material" curve. The latter curve, like the rapid-decay example, passes through a part of the figure that presumably ensures few or no complaints from occupants.

There are of course other approaches to evaluating the impact of emissions. One is to use IAQ models to predict indoor concentrations of pollutants and then incorporate time-activity patterns of people, to calculate exposures (e.g., in micrograms per day inhaled). This is especially relevant for individual pollutants for which dose-response data are available, because health risk estimates can then be calculated (8). Another approach is to use panels of people to judge the acceptability of emissions (4). This can be useful for identifying problematic materials and estimating ventilation requirements to avoid occupant dissatisfaction with odors and irritant emissions, without making chemical measurements.

Summary

A wide variety of surface materials in buildings can release organic compounds. Examples include building materials, furnishings, maintenance materials, clothing, and paper products. These sources contribute substantially to the hundreds of organic compounds that have been measured in indoor air. Their emissions have been directly connected to complaints of odors or hyperreactivity in many buildings, and are presumed to contribute to the problems in many "sick buildings" where the cause is uncertain.

Significant progress has been made in the past decade in developing procedures for measuring emissions from such materials, in controlled experiments where factors affecting emission rates can be determined and quantified. Emissions data are still limited, but are being accumulated gradually by research groups in Europe and North America.

It is clear from the recent data gathered in research and modeling studies that one of the most effective ways to limit indoor concentrations of organic compounds is by limiting the content of volatile compounds in materials that are used in buildings. Limiting the original residual content of such compounds in the materials, or conditioning such materials prior to use in buildings, or (perhaps) conditioning such materials in place before occupancy of a new or renovated building are most likely to prevent excessive indoor concentrations.

We are now at a point where researchers, building designers/ architects, building managers, and manufacturers of materials can begin working together toward a goal of low-emitting materials. One place to start that joint effort is the adaptation of research procedures for emissions testing to more routine procedures for use by industrial manufacturers of materials. Emissions testing by manufacturers can lead to both low-emitting materials and guidelines to consumers on conditioning of materials (e.g., by airing out or cleaning) prior to use.

Researchers in the United States and Canada are now working on consensus research procedures for emissions testing, for adoption by ASTM, a voluntary standards organization. Similar efforts in Europe, if not already underway, may be triggered by an ongoing European-North American interlaboratory comparison of emissions testing procedures being sponsored by the U.S. Environmental Protection Agency and Aarhus University in Denmark.

If emissions testing and product certification procedures are available, and there is sufficient market demand for low-emitting materials driven by indoor air quality concerns, significant reductions of indoor concentrations of vapor-phase organic compounds might be achieved within the next decade.

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